Studies on explosion reaction of monovinyl acetylene gas : IV. Thermal reaction of monovinyl acetylene-oxygen mixture

AUTHOR(S):

Ikegami, Tatsuya

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STUDIES ON EXPLOSION REACTION OF MONOVINYL ACETYLENE GAS

IV. Thermal Reaction of Monovinyl Acetylene-Oxygen Mixture

BY TATSUYA IKEGAMI

The thermal reaction of monovinyl acetylene (MVA)-oxygen mixture was mainly studied at 250~400°C and 230~400 mmHg in the range of 3~17% of oxygen, and was referred simply to the range of large amounts of oxygen (40~60% O_2). The reaction was complex and consisted of polymerization, decomposition and oxidation. Among them the reaction of oxidation was first order with respect to MVA and oxygen. Formaldehyde, as the organic oxide, in the gaseous products was found alone. The reaction mechanism was drawn with the assumption of the formation of MVA peroxide and polymeric MVA peroxide in the initial step.

The isobar and isotherm curves of explosion limits in the monovinyl acetylene (MVA)-air and MVA-O_2 system have particular shape($\cup$), in which the peaks are at 80~90 vol.% of MVA for MVA-air mixture and at 3~5 vol.% oxygen for MVA-O_2 mixture and there are the minimum around at $(O_2/MVA) \fallingdotseq 1$, as described in the previous papers[1][2]. It is presumed that oxygen has different effects on the explosion of MVA. So, studies on the thermal reaction of MVA and oxygen mixture are needed in order to draw the reaction mechanism. Though a lot of literature on the oxidation of C_2H_2[3a][3b] and C_2H_4[4] have been published, no reference on the oxidation of MVA, having the acetylenic and ethylenic bond, are available.

The results in the range of small amounts of oxygen (O_2 3~17 vol.%) are mainly described and those in considerable amounts of oxygen are referred simply in this paper.

Experimentals

Apparatus and procedure were almost similar to those described in the previous paper[2]. *Materials* were almost the same, but MVA contained slightly more impurities (traces of butadiene, vinylchloride, acetone etc.), its purity being more than 99.0%. The experimental results were not affected by these impurities. *Analysis* was performed by the gas chromatograph for gaseous products, but it was not done for solid and liquid products, because it was very difficult to take them out of the reaction vessel rapidly without secondary change. The main column and carrier gas used were almost the same as

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2) T. Ikegami, *This Journal*, 33, 6 (1963)
3a) W. A. Bone and J. F. Carruthers, *Proc. Roy. Roc.*, A162, 502 (1937)
3b) E. W. R. Steacie and R. D. McDonald, *J. Chem. Phys.*, 4, 75 (1934)
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Table 1 Analytical conditions of gas chromatograph

Column bed	Carrier gas	Flow rate ml/min	Temp. C°	Identified peaks
DOP on Celite (2 m) +DNP on Diasolid (2 m)	H_2	60	80	O_2, C_3H_6, HCHO, B***, MVA, (CH_3COCH_3)
Active carbon (2 m)	H_2	40	80	O_2, CO, CH_4, CO_2, C_2H_2, C_2H_6, (C_2H_6)
Active carbon (2 m)	N_2	40	80	H_2, CO, CH_4, CO_2, C_2H_2, C_2H_4
Silica gel (2 m)	H_2	40	140	(O_2), (CH_4), C_2H_6, $C_2H_4+CO_2$, C_3H_8, C_2H_2, C_3H_6, B**, MVA

* B** : C_4H_6 (butadiene)

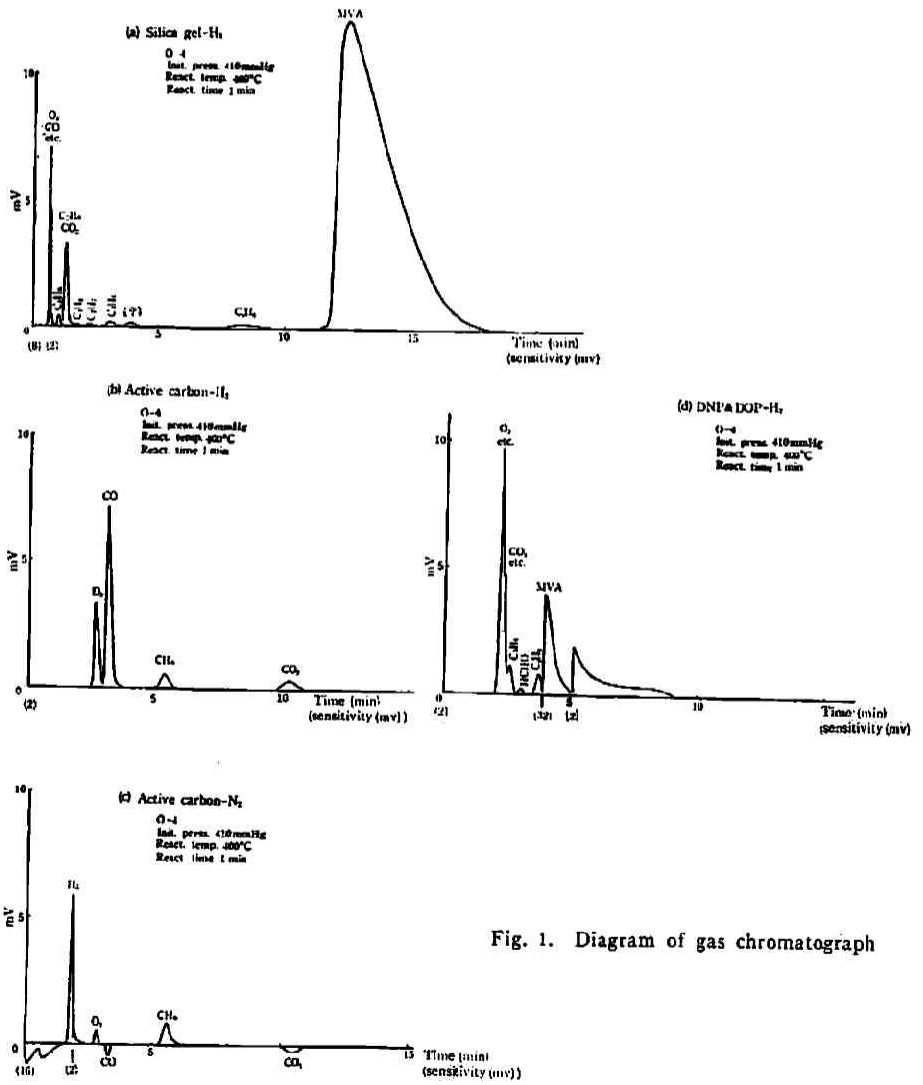


Fig. 1. Diagram of gas chromatograph

those in the previous paper[5]. The (DOP+DNP) column was used, instead of the DOP column, in order to obtain fine separation. Analytical conditions and analyzed products are summerized in Table 1.

The typical charts of analysis are in Fig. 1 a)–d). Though formic acid, acetic acid, hydrogen peroxide, acrolein, propylene oxide, benzene, ethyl alcohol, acetone, methyl alcohol *etc.* were also tested, they were not identified in the reaction products. The TCP-H_2 and PEG 4000-H_2 system were used subsidiarily to obtain more exact analytical data and to confirm the above compounds.

It has been reported that some oxidation reactions of hydrocarbons had different mechanism depending upon the ratio of hydrocarbon to oxygen and the reaction temperature. In the explosion reaction of MVA-O_2 system[2], the explosion limits were found to have a particular shape (ᔕ), consisting of a peak around 5 vol.% of MVA, and competitive reactions of oxidation, polymerization and decomposition were thought to occur. Considering the above results, the two ranges of composition of oxygen were studied in this oxidation reaction of MVA. In the range of small amounts of oxygen (I), 3vol.% of oxygen (O-1), 7.5vol.% of oxygen (O-6) and 17vol.% of oxygen (O-10), being a round peak, were examined. In the range of considerable amounts of oxygen (II), 40 vol.% of oxygen (O-35), 60 vol.% of oxygen (O-50) and 97 vol.% of oxygen (O-97) were done.

The reactions were compared each other under the same conditions as possible in each group. No exact comparison between the two ranges described above was done.

Experimental results and Considerations

Total pressure change-time relation

The total pressure change against time was measured to survey the apparent reaction feature. The results are summerized in Fig. 2 a)–c).

It is observed that the curves of gradual decrease in pressure similar to those in the thermal reaction of MVA[5] are obtained and the rate of decrease in pressure becomes smaller with increasing oxygen content in the range of a small amount of oxygen (O-1 (O_2: 3vol.%), O-4 (O_2: 7.5val.%), O-6 (O_2: 10vol.%) and O-10 (O_2: 17vol.%)). It is suggested that the principal reaction is the polymerization reaction, resulting in the decrease in pressure, and the action of oxygen is to increase the pressure and/or to retard seemingly the polymerization reaction in this range.

In the range of considerable amounts of oxygen, (O-35 (O_2: 40 vol.%), O-50 (O_2: 60 val.%) and O-97 (O_2: 97 vol.%)), the pressure change curves show that the slight pressure decrease or constant pressure is followed by a small pressure rise. These indicate that the decrease in pressure due to polymerization reaction is suppressed or overcome by the increase due to the decomposition and/or the oxidation reaction.

No induction period is found in every experiment in both ranges.

Typical feature of reaction products

It seems to be important for elucidating the reaction mechanism to analyse the reaction products and to find the change of products against time.

5) T. Ikegami, *This Journal*, **33**, 15 (1963)

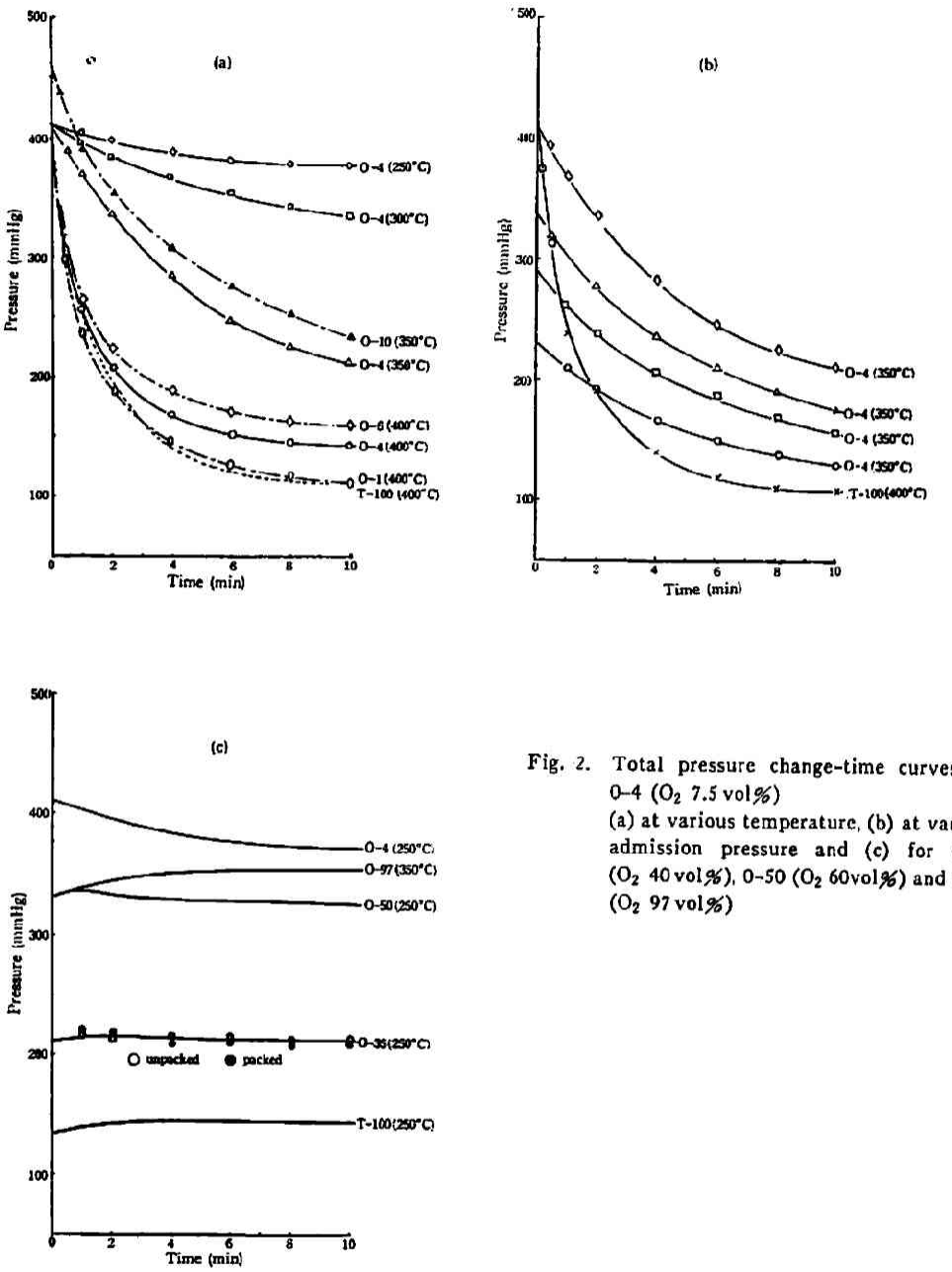


Fig. 2. Total pressure change-time curves for 0-4 (O_2 7.5 vol%)
(a) at various temperature, (b) at various admission pressure and (c) for 0-35 (O_2 40 vol%), 0-50 (O_2 60vol%) and 0-97 (O_2 97 vol%)

The analyzable gaseous compounds in the oxidation reaction of MVA were, (1) MVA, (2) oxygen, (3) hydrogen, (4) CO, (5) CO_2, (6) HCHO, (7) CH_4, (8) C_2H_6, (9) C_2H_4, (10) C_2H_2, (11) C_3H_8, (12) C_3H_6, (13) butadiene (H_4H_6) etc., each being identified and measured quantitatively, and some other compounds, not confirmed, (presumed to be C_4 compounds and lower polymer).

Formaldehyde (HCHO) was found alone as organic oxide among the oxidized compounds formed.

The amounts increase with increasing the content of oxygen.

The feature of the main products in O-4 (O_2: 7.5 vol.%) at 400°C (reaction temperature) and 410 mmHg (initial pressure) is shown in Fig. 3. The ordinate is indicated by the mole ratio against the initial MVA with the exception of oxygen, being shown against the initial oxygen. Every curve is smooth and has no peak and no valley during this period. This is similar to the thermal reaction of MVA[5]. Variety of compounds and relative amounts are also similar to those in the thermal reaction of MVA, with the exception of the oxidized products such as CO, CO_2 and HCHO.

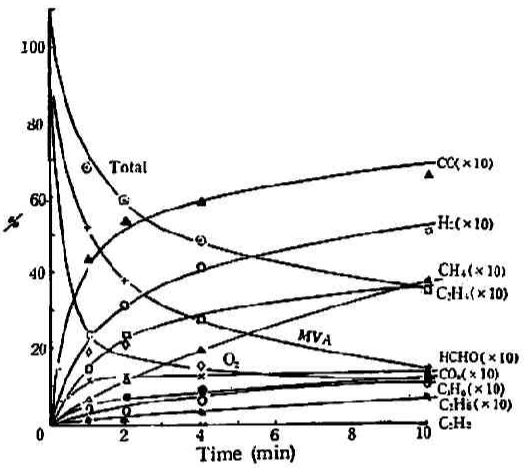


Fig. 3. Product change-time curves for O-4 (O_2 7.5 vol. %) 400°C, 410 mmHg (MVA 380mmHg)

The consumption of MVA is larger than that of oxygen in amounts, and continues to proceed even after the consumption of oxygen is stopped. This indicates that the polymerization is principal in 7.5 vol.% of oxygen (O-4).

Effect of pressure and temperature

The effect of the initial pressure at the constant temperature (350°C) was investigated on O-4 (O_2: 7.5 vol.%) in the pressure range of 230～410 mmHg. Any big difference is not found on the shape of curve and on relative amounts of compounds at any time as seen on the change of MVA and oxygen, (Fig. 4(a)), and CO and CO_2 (Fig. 4(b)). Concerning the other compounds formed, the similar results are obtained.

The effect of temperature on O-4 (O_2: 7.5 vol.%) was studied at the constant initial pressure (410 mmHg) in the range of 250～400°C. The amounts of compounds, produced and consumed at any time, depend upon the reaction temperature very much as shown in Fig. 5 (a)–(c). The curves against time show gradual increase or decrease.

As gradual decrease or increase is found in the consumption of MVA and oxygen and in the formation of various compounds, it does not seem to give a serious trouble (error) to see the effect of temperature and pressure using the results at the reaction of 10 minutes. The results obtained by changing admission pressure at the definite temperature (350°C) are shown in Fig. 6 (a). Those with respect to temperature are in Fig. 6 (b). Though the main products are not affected by the admission pressure in the range of 240～410 mmHg with the exception of C_3H_6 and CH_4, the large effect of the

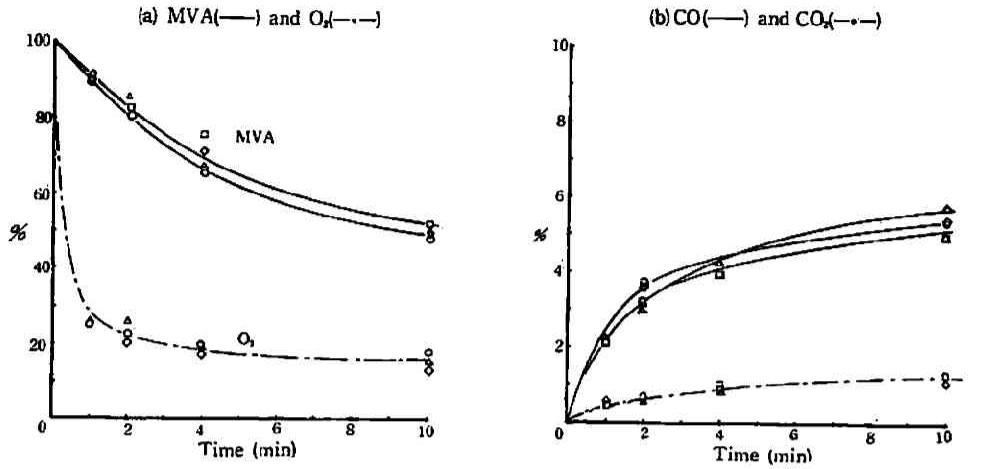


Fig. 4 Yield-time for 0–4 (O_2 7.5 vol%) at constant temperature (350°C) and various initial pressure
410 mmHg(○), 340 mmHg(△), 290 mmHg(□), 230 mmHg(◇)

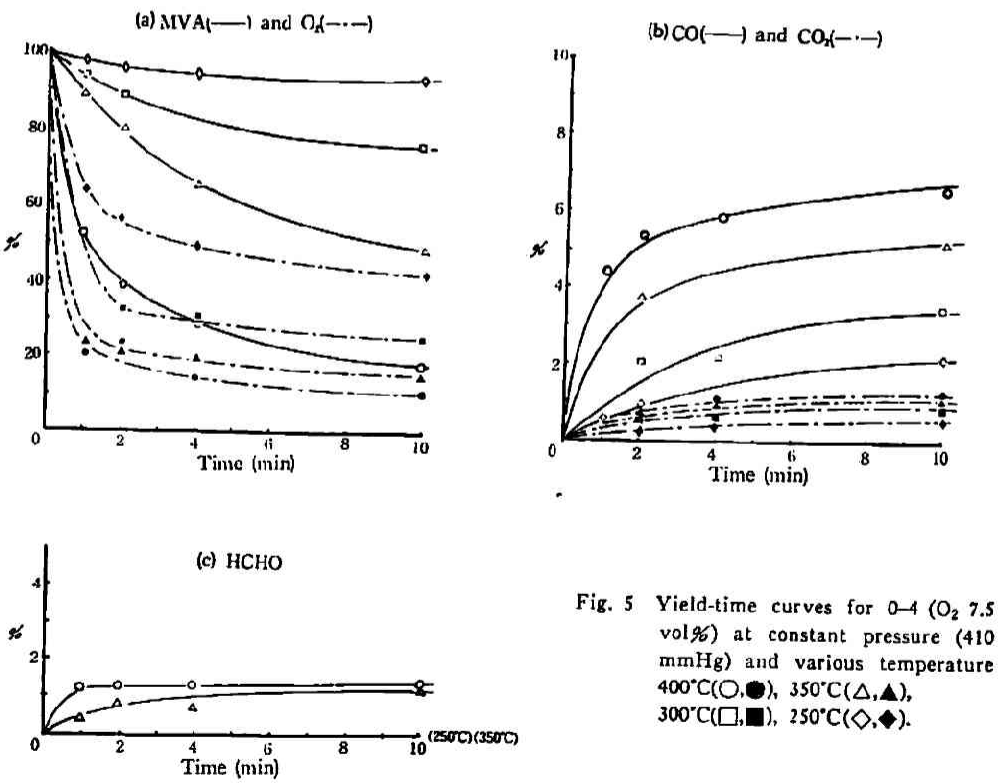


Fig. 5 Yield-time curves for 0–4 (O_2 7.5 vol%) at constant pressure (410 mmHg) and various temperature
400°C(○,●), 350°C(△,▲),
300°C(□,■), 250°C(◇,◆).

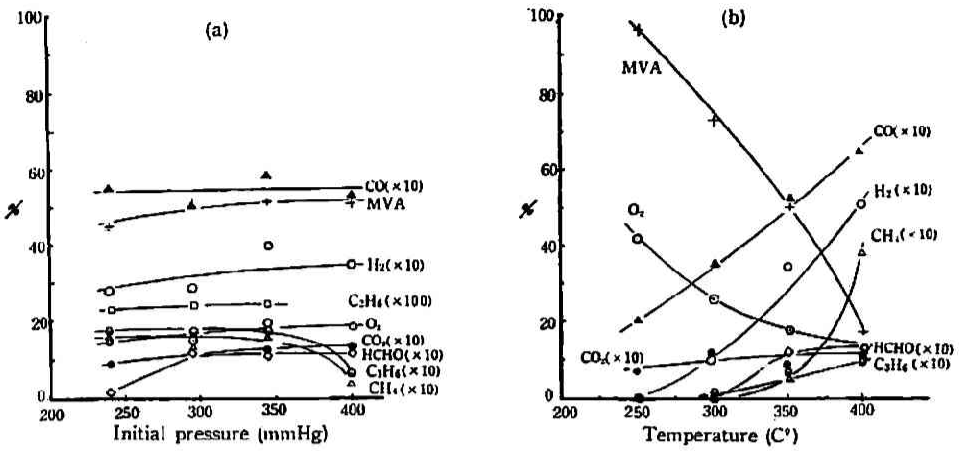


Fig. 6 Yield-time for 0-4 (O_2 7.5 vol %) at 10min.
(a) at various initial pressure (350°C) and
(b) at various temperature (410mmHg)

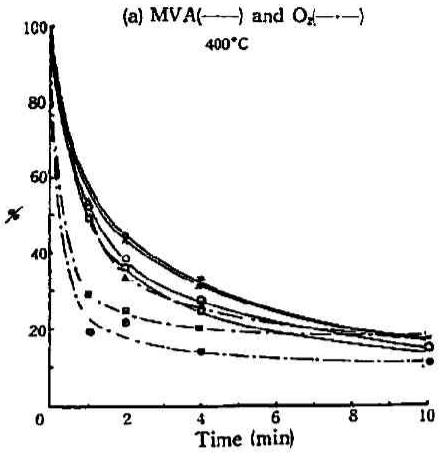
reaction temperature is found as seen in Fig. 6 (b). The consumption of MVA and oxygen increases almost linearly with rising temperature, while CO and CO_2 are found to be produced considerably even at 250°C. CH_4, H_2, C_3H_6, C_2H_4 etc. start to form in about 250~300°C and increase the amounts rapidly with rising temperature. HCHO appears over 300°C. C_2H_2 is not found even at 400°C. In comparison with the thermal reaction of MVA[5], the existence of oxygen suppresses the pressure effect on the production of CH_4, H_2 etc. and accelerates the consumption of MVA even at low pressure, but retards it at high pressure.

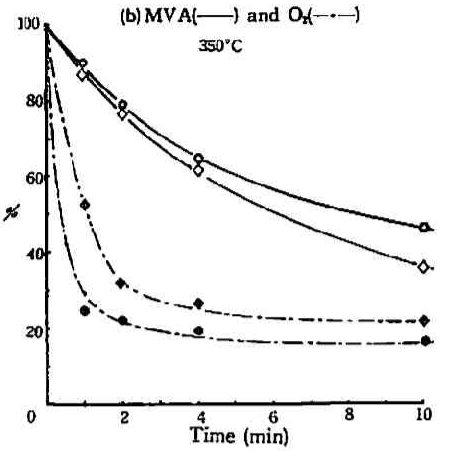
Effect of composition

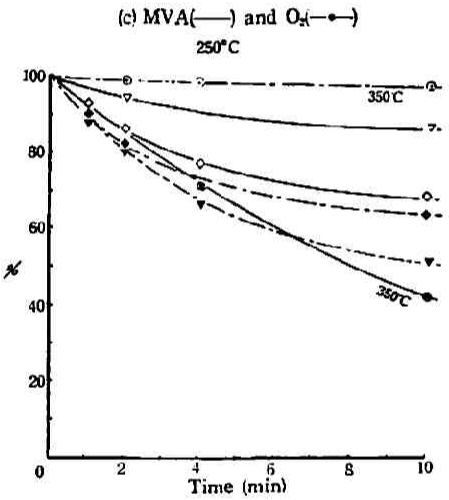
The effect of composition was tested by a series of experiments, in which MVA was kept at almost constant pressure and the pressure of oxygen varied, in the ranges of small amounts of oxygen content (I) and considerable amounts of oxygen (II). The conditions used in the range of (I) were 400°C and 350°C for the reaction temperature, about 390 mmHg for the initial partial pressure of MVA and 0 vol.% of oxygen (T-100), 3 vol.% of oxygen (O-1), 7.5 vol.% of oxygen (O-4), 10 vol.% of oxygen (O-6) and 17 vol.% of oxygen (O-10) as the content of oxygen. The results obtained are summerized in Fig. 7 (a)-(m). In the range of considerable amounts of oxygen (II), 40 vol.% of oxygen (O-35) and 60 vol.% of oxygen (O-50) were used at 250°C and 130 mmHg of partial pressure of MVA, and 97 vol.% of oxygen (O-97) were tested additionally.

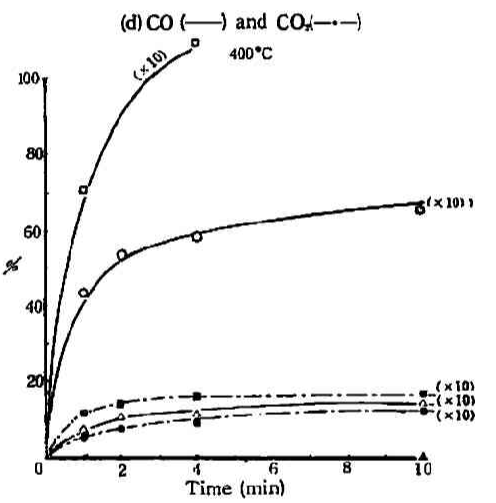
The consumption rate of MVA and the formation of its oxides (CO, CO_2 and HCHO), in general, increase according to the content of oxygen in both ranges. HCHO was found even at low temperature in the range of considerable amounts of oxygen. On the other hand, the inverse phenomenon is found in the consumption of oxygen.

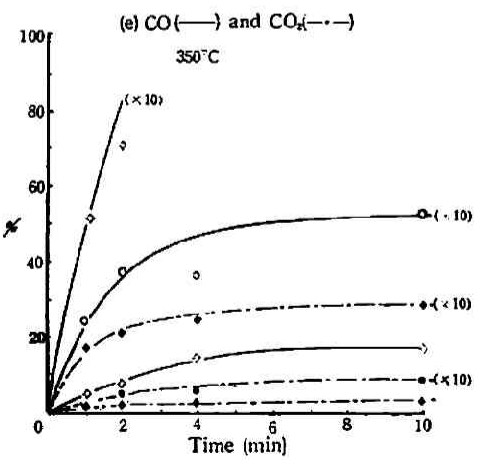
In the range of small amounts of oxygen, the consumption of MVA in 3 vol.% of MVA (O-1) is slightly less than that in the absence of oxygen (T-100). It seems to suggest that small amounts of oxygen retards the polymerization reaction.

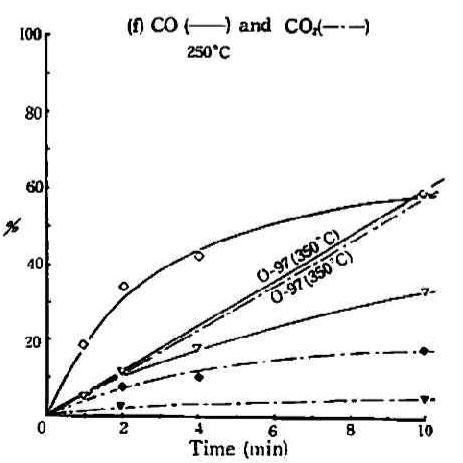

(a) MVA(——) and O₂(—·—)
400°C
%
Time (min)


(b) MVA(——) and O₂(—·—)
350°C
%
Time (min)


(c) MVA(——) and O₂(—•—)
250°C
350°C
350°C
%
Time (min)


(d) CO (——) and CO₂(—·—)
400°C
(×10)
(×10)
(×10)
(×10)
(×10)
%
Time (min)


(e) CO(——) and CO₂(—·—)
350°C
(×10)
(×10)
(×10)
(×10)
%
Time (min)


(f) CO (——) and CO₂(—·—)
250°C
O-97(350°C)
O-97(350°C)
%
Time (min)

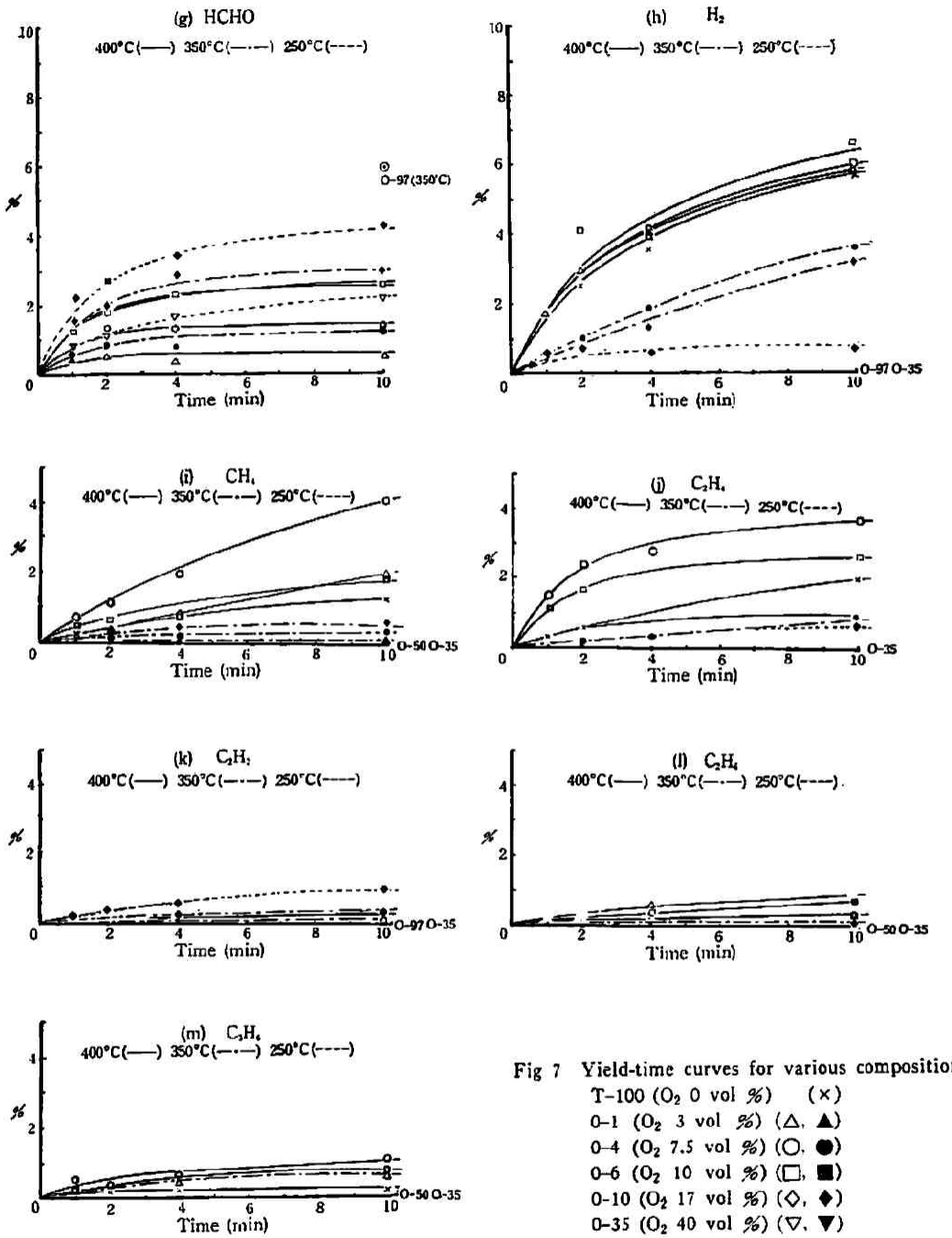


Fig 7 Yield-time curves for various composition

T-100 (O_2 0 vol %) (×)
0-1 (O_2 3 vol %) (△, ▲)
0-4 (O_2 7.5 vol %) (○, ●)
0-6 (O_2 10 vol %) (□, ■)
0-10 (O_2 17 vol %) (◇, ◆)
0-35 (O_2 40 vol %) (▽, ▼)
0-50 (O_2 60 vol %) (◇, ◆)
0-97 (O_2 97 vol %) (⊗, ⊙)

On the formation of hydrogen and hydrocarbons, the definite order is not found with respect to the oxygen content. This appears to be based on the secondary reaction with oxygen.

Relations among products

Various ratios among the products were calculated to draw out the reaction mechanism.

Oxides and hydrocarbons. The following table (Table 2) is given as the typical examples to see the percentage of oxides and hydrocarbons in the gaseous products. The material balance is found to be fairly good from the table within experimental errors in the gas chromatographic analysis.

Table 2 Material balance of gaseous products

		T-100		0-1		0-4					0-6		0-50		0-35		0-4	
Reaction temperature (°C)		400		400		400					400		250		250		250	
Reaction time (min)		0	10	0	10	0	1	2	4	10	0	10	0	10	0	10	0	10
Reading pressure (mmHg)		400	106	400	110	410	255	205	166	133	413	155	330	327	210	210	410	375
Analytical	Oxides	0	0	0	7.3	0	20.5	26.6	27.0	31.0	0	33.7	0	108	0	53.0	0	10.6
	H_2 and hydrocarbons	0	37.2	0	42.2	0	17.8	25.4	42.0	47.0	0	45.4	0	2.6	0	≒0	0	≒0
	MVA	400	68.0	388	66.0	380	197	140	110	55.2	375	67.5	132	90.0	126	110	380	352
	O_2	0	0	12.0	1.4	30.0	6.6	6.0	4.5	3.1	38.0	12.0	198	127	84	44.0	30.0	12.0

It is observed that hydrocarbons and hydrogen slightly increase with increasing oxygen content, and their formations are very little compared with the consumption of MVA in the range of small amounts of oxygen and at high temperature. Hydrocarbons and hydrogen are thought to be mainly produced by the pyrolysis of MVA, because their yields are almost the same amounts as those in the absence of oxygen.

Gaseous products and solid and liquid products. The balances of oxygen, carbon and hydrogen were calculated to obtain the ratio of gaseous products to polymer products.

Unfortunately, it was impossible to determine the exact amounts of polymer, since they could not be analyzed. Then, the differences between the contents of oxygen, carbon and hydrogen in the gaseous products and their contents in the initial MVA were observed.

The 'differences' on the carbon balance means the sum of carbon deposited and products unidentified, such as polymer. As their amounts are thought to be very little, considering the material balance, so the difference described above may be mainly due to polymer products.

The resuls calculated are shown in Table 3. The differences are indicated by "others". It seems that some polymers contain oxygen even in the range of considerable amounts of oxygen. The ratio of gaseous products to "others" slightly increases with time.

CO/CO_2. The ratio of CO to CO_2 is an important factor to elucidate the mechanism. However, the constant value can not be obtained. CO/CO_2 reduces, in general, with time. This means that the oxidation to CO_2 occurs in the later stage.

Table 3 Balance of carbon, oxygen, and hydrogen in gaseous, liquid and solid products

		T-100	0-1	0-4				0-6	0-4	0-35				0-50
Reaction temperature (°C)		400	400	400				400	250	250				250
Reaction time (min)		10	10	1	2	4	10	10	10	1	2	4	10	10
Oxygen balance	Gaseous (%)	/	35.0	49.5	56.0	71.0	87.0	55.0	50.0	64.0	53.0	65.0	73.0	92.0
	Others (%)	/	65.0	50.3	44.0	29.0	13.0	45.0	50.0	36.0	47.0	35.0	27.0	8.0
Carbon balance	Gaseous (%)	2.5	4.2	5.2	5.7	7.0	7.5	6.7	47.0	63.0	63.0	70.0	80.0	68.0
	Others (%)	97.5	95.8	94.8	94.3	93.0	92.5	93.3	53.0	37.0	37.0	30.0	20.0	32.0
Hydrogen balance	Gaseous (%)	8.7	13.9	8.7	10.3	13.1	17.3	9.3	/	13.3	11.0	10.6	10.0	9.5
	Others (%)	91.3	86.1	91.3	89.7	86.9	82.7	90.7	/	86.7	89.0	89.4	90.0	90.5

T-100 : O_2 0%, 0-1 : O_2 3.5%, 0-4 : O_2 7.5%
0-6 : O_2 10%, 0-35 : O_2 40%, 0-50 : O_2 60%
"Others" in oxygen balance contain H_2O and polymer
"Others" in hydrogen blance contain H_2O and polymer
"Others" in carbon balance contain deposited carbon, and polymer

Effect of surface area

Though the effect of the surface area was not investigated systematically, the results obtained in a series of 0~35 (O_2 : 40 vol.%) using a packed tube, the surface area of which is 2.5 times as large as the former tube are shown in Fig. 2 (c) and Table 4.

Table 4 Reaction products in the reaction using packed vessel (Reaction period 2 min. Temp. 250°C. Init. pressure 210mmHg O_2 40% MVA 60%)

	O_2	MVA	H_2	CO	CH_4	CO_2	HCHO
Packed (%)	75.0	94.7	0.0614	4.35	0	1.93	0.707
Unpacked (%)	80.2	95.0	0.081	9.31	0	1.62	1.050

The apparent total pressure change against time seems to be almost the same or to be slightly lower. Each product formed is also the same.

Products of explosive reaction

It is of interest to describe the reaction products just below or above the explosion limit of temperature. The explosion reaction in MVA-oxygen system had so short an induction period (less than 10 seconds), that it was very difficult to obtain the change of products against time. Then, the products were taken out at 20 seconds after the admission. The results are shown in Table 5.

The distinguished phenomena of the explosion reaction are the formation of a lot of carbon, C_2H_2 and hydrogen. The amount of consumed oxygen is not changed very much just below and above the explosion limit of temperature, but it is rapid.

Table 5 Reaction products on explosion
(20sec. after admission)

Sample	Temp. (°C)	I. P.* (sec)	Pressure (mmHg) Initial	Pressure (mmHg) Final	Explosion	Reaction products (%)** O_2	MVA	H_2	CO	CH_4	CO_2	C_2H_2	C_2H_4	C_3H_6	HCHO
O-4	418	–	410	275	no	21.8	53.7	1.04	4.63	0.119	0.832	0	1.19	0.482	0.984
	425	2.40	410	480	yes	22.6	26.7	30.1	7.21	11.7	0.625	24.3	8.54	0	0.872
O-10	365	–	460	412	no	36.6	85.6	0.40	4.93	0.141	2.30	0	0	0.399	1.00
	370	1.27	460	584	yes	21.2	36.0	46.2	20.3	11.2	0.75	24.3	6.66	0	0.79
T-100	413	–	460	360	no	–	77.0	1.23	–	0.313	–	t***	t	t	–
	416	5.87	460	520	yes	–	31.5	50.3	–	14.3	–	16.5	7.82	3.14	–

* I. P.: induction period
** O_2 is indicated by mole ratio to initial O_2, others are mole ratio to initial MVA
*** t: trace

Order of reaction, apparent activation energy

The order of reaction in the oxidation reaction of MVA was determined, applying the isolation method, the differential method and the modified half period method. MVA or oxygen may be thought to be very excessive in 97 vol.% of MVA (O-1) or 97 vol.% of oxygen (O-97). So, the time at which one tenth of the amount of oxygen or MVA was consumed was estimated by the consumption curve of oxygen or MVA in Fig. 7 (a) and Fig. 7 (c). According to the results, the constant time is obtained in the course of reaction. These mean that the reaction rate is first order with respect to MVA or oxygen in the early stage.

However, the consumption of MVA is also so rapid in the O-1 (O_2 : 3 vol.%) that there is some doubt on the apparent constancy of MVA concentration. Then, the order of reaction with respect to oxygen was determined, using the differential method. The order of reaction with respect to oxygen was determined by the measurements of the initial rates of a series of experiments, in which MVA was maintained at the constant pressure, and the pressure of oxygen varied. The initial rates were obtained on the curves of oxygen consumption in Fig. 7 (a) and (c).

Fig. 8 shows the plots of the logarithm of the initial pressure of oxygen against the corresponding initial rate. From the slope obtained, it is confirmed that the rate of reaction depends approximately upon the first order of oxygen in both ranges of (I) (small amounts of oxygen) and (II) (considerable amounts of oxygen).

The order of reaction obtained by the same method, using d(CO)/dt as the reaction rate, is approximately first order with respect of oxygen as seen in Fig. 8.

Activation energy was obtained from the slope of the plots of the logarithm of the initial rate against ($1/T°K$) for a series of O-4 (O_2 : 7.5 vol.%) as seen in Fig. 9, the composition of the initial mixture being the same in each case. The experimental activation energy is determined as about 10 k cal/mole and the rate expression has the form :

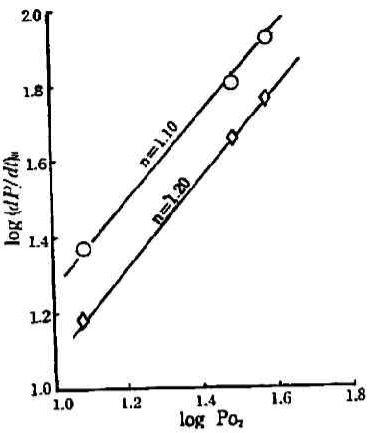


Fig. 8 Dependence of the rate upon oxygen pressure at 400°C
Rate : $-d(O_2)/dt$ (○)
$d(CO)/dt$ (◇)

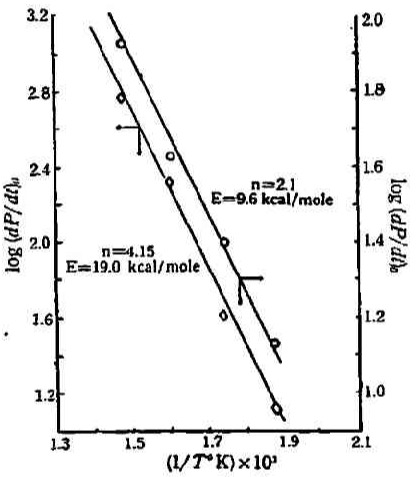


Fig. 9 Effect of temperature on reaction rate for 0-4 (O_2 7.5 vol %) series.
Rate : $-d(O_2)/dt$ (○)
$d(CO)/dt$ (◇)

$$k=0.76\times 10^{4}\exp(-10{,}000/RT)\ 1\ mole^{-1}\ sec^{-1}.$$

This value of the activation energy seems to be abnormally low, comparing with about 30 k cal/mole obtained from the explosion limits in the previous paper[2].

The apparent activation energy obtained with use of d(CO)/dt is 19.0 k cal/mole and is higher than the above.

Reaction mechanism

As the thermal reactions in the MVA-oxygen system include oxidation, decomposition and polymerization reaction of MVA, and are very complex, it can not be concluded that only the oxidation reaction proceeds in the above system.

So, some presumable considerations are mentioned on the mechanism of the oxidation reaction of MVA. The presence of a double and/or a triple bond in the fuel molecule may occur in two steps[6a)6b)]

6a) O. F. H. Tipper, *Quat. Rev.*, 11, 313 (1957)

6b) G. J. Minkoff and C. F. H. Tipper, "*Chemistry of Combustion Reaction*", Butterworths Sci. Pub. London (1962)

in the initial stage. (1) addition to the double bond and/or triple bond may occur, or (2) hydrogen abstract may give radicals as below

$$\text{(addition)}\quad RH+O_2 \longrightarrow ROOH \tag{1}$$

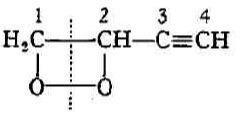
$$\text{(hydrogen abstraction)}\quad RH+O_2 \longrightarrow R+HO_2 \tag{2}$$

Reaction (2) is generally endo-thermic* and its activation energy would be very high in the gas phase. Reaction (1) would be favored with ethylene and acetylene.

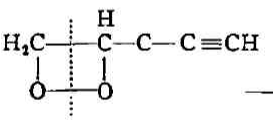
MVA ($CH_2=CH-C\equiv CH$) have a double and a triple bond. The reaction with oxygen would be very complex. The results obtained in the thermal reaction of MVA and oxygen in this experiment show that (1) the reaction rate is the first order with respect to MVA and/or oxygen, (2) the activation energy obtained from $-d(O_2)/dt$ is about 10 kcal/mole, being very low and (3) in the oxidation products aside from CO and CO_2, HCHO is found alone, and not the cyclic oxides, such as C_2H_4O and C_3H_6O. So, the addition reaction would be favored and MVA peroxide would be formed in the initial step, considering the easy formation of their peroxide of butadiene[7a] ($CH_2=CH-CH=CH_2$) or other dienes[7b], having similar structure, with oxygen,

$$C_4H_4+O_2 \longrightarrow C_4H_4O_2 \tag{3}$$

The structure of $C_4H_4O_2$ would have

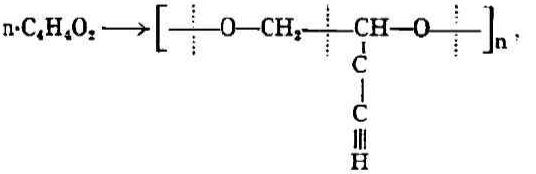


with 1, 2 addition of oxygen because HCHO is found alone in organic oxides. The MVA peroxide would decompose to form HCHO and CH≡C—CHO by the cleavage of (O–O)** bond and (C–C)** bond at 1, 2 position.



$$\longrightarrow HCHO+CH\equiv C-CHO, \tag{4}$$

or would rapidly polymerize to produce the polymeric peroxide as in the case of the diene[7],



$$\tag{5}$$

or would initiate the polymerization of MVA in the excess of MVA as seen in the usual polymerization

$$n\cdot C_4H_4O_2+m\cdot C_4H_4 \longrightarrow (C_4H_4O_2)_n(C_4H_3)_m. \tag{6}$$

* The endothermicities of reaction (2) are over 60 kcal/mole in the case of ethylene or acetylene[6a,n].

** The bond dissociation energy of (O–O) and (C–C) in MVA peroxide are not exactly given, but it is presumed that (O–O) is weak and would be about 40 kcal, considering 34 kcal for dibutylperoxide. (C–C) of 1, 2 position is thought to have less bond energy than other (C–C) and (C–H).

7a) C. T. Handy and H. S. Rothrock, *J. Am. Chem. Soc.*, **80**, 5306 (1958)

7b) A. V. Tobolsky & R. B. Mesrobian, "*Organic Peroxide*", Interscience Pub., New York (1954)

Oxygen would be contained in the polymer products from aspects of carbon, oxygen and hydrogen balance, and the formation of HCHO increases with rising temperature. The polymeric peroxide would easily decompose. as seen in polymeric diene peroxide[7], to form HCHO and CH≡C—CHO by the splitting of (O–O) bond and (C–C) bond of 1, 2 position.

Propargyl aldehyde (CH≡C—CHO) would be so unstable at high temperature that it would easily decompose and/or be oxidized with oxygen to form carbon, CO etc.

Formaldehyde is also competitively oxidized with oxygen to produce CO, CO_2 and H_2O. That the activation energy (about 20 k cal/mole) obtained from d(CO)/dt is similar to that in the oxidation of HCHO[8] may support the above consideration.

The reaction taking place in the explosion must be examined considering polymerization, oxidation and decomposition reactions in the MVA-oxygen system as described in the thermal reaction.

In the presence of large excess of MVA, the polymerization reaction of MVA is still main and heat of reaction evolved results in explosion. However, the presence of small amounts of oxygen (within a few per cent) inhibits or retards the reaction of polymerization. In a series of 3 vol.% of oxygen (0-1) the consumption rate of MVA is slightly retarded compared with that in the absence of oxygen. The curves of isotherm and isobar of the explosion limits[2] have a peak at the composition. Over such content of oxygen, both reactions of oxidation and polymerization are competitive to accelerate the consumption of MVA. The explosion limits are lowered. The heat needed for the explosion are afforded very much by the polymerization and oxidation of MVA.

In the range of more oxygen content, the oxidation reaction of MVA takes on a main roll. The higher rate of oxidation lowers the explosion limits.

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The Kanegafuchi Chem. Ind. Co., Ltd.
Osaka, Japan

8) R. Fort and C. N. Hinshelwood, *Proc. Roy. Soc.*, A129, 284 (1930)